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(54) Title : PROCESS FOR PRODUCING A SLOW-RELEASING ZINC FERTILIZER

(57) Abstract :

A new type of slow-releasing zinc fertilizer has been developed based on a short chain polyphosphate structure. This compound has low solubility in water but high solubility in dilute acid and organic complexants; they are dry and powdery in nature. The process for synthesis involves heating zinc oxide with phosphoric acid at 300°C followed by neutralisation with a basic compound. By and large, the zinc polyphosphate fertilizer is expected to provide a genuinely slow-releasing zinc fertilizer that is affordable, easy to produce, environmentally safe and widely applicable.

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THE PATENTS ACT. 1970

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Specification

SECTION 10

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

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This invention relates to a process for the manufacture of slow-releasing zinc fertilizer comprising of zinc polyphosphate compounds. According to the process of the present invention, zinc oxide is heated with phosphoric acid to produce low molecular weight polyphosphates, which is subsequently treated with basic compounds to convert it to the desired form. The product, which is either calcium-zinc polyphosphate or ammonium zinc polyphosphate can be readily used as a zinc fertilizer.

Compounds which are widely used today as zinc fertilizers are mostly soluble salts of zinc such as zinc sulphate, zinc-EDTA, etc. and liquid fertilizers such as a solution of zinc in condensed phosphoric acid or ammonium polyphosphate (V. Sauchelli, 1967, Chemistry and technology of fertilizers, Reinhold, New York; G.H. Collins, 1955, Commercial fertilizers, McGraw Hill, New York). The synthesis of zinc fertilizers of low water solubility have also been described in Australian patent 326160 and US Patent 3574591. In both these processes, the phosphates are heated to fusion temperatures and then rapidly cooled, thereby resulting in the formation of glasses.

The major drawbacks of using soluble salts as micronutrient fertilizers are, rapid leaching losses, ground water contamination and the possibility of toxicity, since the dosage requirements are usually very low. On the other hand micronutrient fertilizers having reduced water solubility do not suffer any of these disadvantages. Moreover, a constant supply of nutrient is available to meet the requirement of the crop at all stages of its growth.

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In spite of these advantages the production of phosphate glass frits on a large scale has not attained the desired degree of popularity. This is mainly due to the high temperatures that are employed and which necessitates the use of platinum containers or similar expensive materials that can resist the extremely corrosive nature of phosphoric acid at temperatures above 400°C. The present invention eliminates this difficulty by producing a nonglassy zinc polyphosphate powder at much lower temperatures, so that the corrosive action of phosphoric acid is greatly reduced and inexpensive raw materials such as ceramic-ware can be used as containers. The energy input required is also much lower.

The present invention provides a process for the manufacture of slow-releasing zinc fertilizer, which process comprises (a) heating zinc oxide with phosphoric acid of concentration between 30% and 60% P_2O_5 at 150°C, (b) further heating at 300°C, (c) mixing the resultant mass with water, (d) treating with a basic compound such as herein described and (e) finally obtaining a dried powder.

Accordingly, this invention provides a process for producing zinc polyphosphate compounds which are water-insoluble, nontoxic, nonhygroscopic and contain zinc in a completely available form. The main novel feature of this invention is the use of phosphoric acid at fairly low temperatures, to produce low molecular weight

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zinc polyphosphates. Another novel feature is the elimination of hygroscopicity and reduction of water solubility of the aforementioned zinc polyphosphate by treatment with ^{any} basic compound such as lime, sodium carbonate, sodium hydroxide etc. calcium carbonate, ammonia, ^{the} synthesis of short chain polyphosphates rather than long chain polyphosphates such as the glasses, ensures that the zinc remains in a readily available form. However such small chain polyphosphates have a large percentage of their zinc in a water soluble form and are also very sticky and hygroscopic. Treatment with a basic compound removes both these drawbacks.

The principle underlying the production of slow-releasing zinc fertilizer according to the process of the present invention, is that, when zinc oxide is heated with phosphoric acid, initially zinc dihydrogen phosphate is formed. Subsequently, several such molecules polymerise to form linear polyphosphate chains. The Zn^{2+} as well as H^+ ions are bound to the oxygen atoms along the chain. When the chain length is small the number of H^+ ions is proportionately higher and consequently the compound is soluble. As polymerisation increases, more H^+ ions are lost by dehydration and thereby the molecules become more insoluble. In very long chain zinc polyphosphates, the zinc is not readily available to plants. In molecules of smaller chain-length the Zn may be solubilised by complexing agents such as citric acid or EDTA and is therefore readily assimilable by plants. However during

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the synthesis of polyphosphates, since a range of chain lengths is invariably obtained, a part of the product exhibits water solubility due to the presence of small sized chains. This problem has been resolved here, by further reacting the zinc polyphosphate residue with ammonia, calcium carbonate, calcium oxide or similar materials, so that the excess H^+ ions in the short chain molecules, as mentioned above, are neutralised. This treatment causes the water soluble molecules to become almost insoluble. It also results in decrease in hygroscopicity of the sample which is therefore convertible to a dry white powder.

Zinc oxide and phosphoric acid are allowed to react at $150^{\circ}C$ to form the dihydrogen phosphate. This is then heated at $300^{\circ}C$ till zinc polyphosphate of the desired degree of polymerisation is produced. The reacted mass is subsequently mixed with water and ammonia, calcium carbonate or calcium oxide are added till the pH of the suspension attains a value of around 3.0. Finally the product is dried and ground to a powdery form. The various stages in the production of the slow-releasing zinc fertilizer are described in detail below.

Zinc oxide powder containing upto 79% Zn may be used as the starting material. Every 100 g of ZnO is treated with phosphoric acid containing **175 g** P_2O_5 . Almost any grade and dilution of the acid can be used for the reaction. Commercial acid of

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30-40% P_2O_5 is quite suitable, though synupy acid containing 60% P_2O_5 , is optimum. The mixture of ZnO and H_3PO_4 , taken in a porcelain crucible, is heated in a furnace at $150^\circ C$ for 30 min. At lower temperatures removal of free water from the mixture may be difficult to achieve. At higher temperatures, polymerisation of the phosphoric acid may occur, causing incomplete conversion of ZnO to zinc phosphate. Therefore a digestion temperature of $150^\circ C$ is optimum. The digested mass, which now contains zinc dihydrogen phosphate, is heated at $300^\circ C$ for 1 hour. Polymerisation of the $Zn(H_2PO_4)_2$ occurs and the resulting polyphosphate has an average chain length (\bar{N}) of 2.35. The total weight lost by the mixture after polymerisation is 11.7% of the total weight of $ZnO + H_3PO_4$. Heating at higher temperatures, above $350^\circ C$ causes a very rapid polymerisation. Controlling the degree of polymerisation at the desired level, therefore becomes very difficult. At temperatures below $250^\circ C$, polymerisation is very slow. Therefore $300^\circ C$ is the optimum temperature for the synthesis of the zinc polyphosphate although any temperature within $250^\circ - 350^\circ C$ may be employed, if necessary. The reaction product obtained after heating at $300^\circ C$, is cooled to room temperature and then ground after the addition of water, so that a slurry is formed. To this 100 g $CaCO_3$ or 56 g CaO or ammonia solution containing 34 g NH_3 is added and the slurry mixed well and allowed to stand for 6 hours to ensure complete reaction. The final pH of the slurry should be around 3.0. Increasing the pH above 3.0 by addition of excess bases may cause

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precipitation of zinc hydroxide. On the contrary, addition of too little of the basic compound causes incomplete neutralisation of the free acid. This results in higher water solubility of the compound and also greater hygroscopicity, both of which are undesirable characteristics. After neutralisation, the slurry is dried and ground to a powder.

The characteristics of this fertilizer are as follows. The sample which has been neutralised with ammonia is a zinc-ammonium-polyphosphate and has the composition 23.8% Zn, 23.1% P and 5.2% N. That, which has been neutralised with calcium compound is a zinc calcium polyphosphate and has the composition 21.68% Zn, 19.1% P and 10.11% Ca. The soluble Zn percentage in these compounds are 7.5% and 1.25% respectively for the ammonium and the calcium forms. Both these samples are 100% soluble in 0.1 N HCl, 1 N citric acid, 1 N ammonium citrate at pH 8.5, 0.02 M EDTA at pH 4.05. As all these aforementioned reagents are used for assessing the availability of zinc, the tests indicate that the zinc in these fertilizers is completely available to plants. Plant growth experiments using traditional zinc fertilizers as well as the fertilizers described herein, also indicate that plant growth and increase in yield of the latter are comparable to those of the former.

Example I

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Zinc oxide powder (100 g) was taken in a porcelain dish and **377 g** of phosphoric acid containing 46.4% P_2O_5 was added. The weight of the mixture was recorded. From this, the calculate weight of $ZnO + H_3PO_4$ (excluding the excess water in the acid and the weight of the crucible) was **341 g**. It was then heated in an electric furnace at $150^{\circ}C$ for 30 min. At the end of this period the temperature of the furnace was increased to $300^{\circ}C$ and the heating was continued at this temperature for 1 hour. The final weight of the sample was **301 g**. If, after heating, the weight of the sample is observed to be higher, then the heating is continued till the weight loss corresponds to about 11.7% of the original weight of $ZnO + H_3PO_4$. Once the period of heating is calibrated for a particular furnace and for a particular type of container and amount of sample, then all subsequent samples can be heated for that period; recording the initial and final weights is, then, not necessary.

After heating at $300^{\circ}C$ the sample was taken out of the furnace and cooled to room temperature. 250 ml water was added and the sample was then ground to a thin paste. Subsequently 100 g $CaCO_3$ was added to it and mass was mixed thoroughly. After about 6 hrs the product was dried and powdered. The material thus obtained has the composition **21.68% Zn**, 19.1% P and **10.11% Ca**.

Example II

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The entire process was the same as in example I except that during neutralisation 56 g CaO was used instead of CaCO_3 . The composition of this sample was the same as that in example I.

Example III

The entire process was the same as in example I except that during neutralisation ammonia solution was used instead of calcium carbonate. To the slurry described above, 340 ml ammonia solution containing 10% NH_3 was added, mixed thoroughly and the end product obtained as described in example I. The composition of this sample was 23.8% Zn, 23.1% P and 5.2% N.

We claim :

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1. A process for the manufacture of slow-releasing zinc fertilizer, which process comprises (a) heating zinc oxide with phosphoric acid of concentration between 30% and 60% P_2O_5 at $150^{\circ}C$, (b) further heating at $300^{\circ}C$, (c) mixing the resultant mass with water, (d) treating with a basic compound such as herein described and (e) finally obtaining a dried powder.
2. A process as claimed in Claim 1 wherein the phosphoric acid used has any concentration between 30% and 60% by weight P_2O_5 .
3. A process as claimed in any of the preceding claims wherein at stage (a) zinc oxide is heated with phosphoric acid at $150^{\circ}C$.
4. A process as claimed in any of the preceding claims wherein at stage (b) the reaction is carried out at any temperature within^a range $250^{\circ}-350^{\circ}C$.
5. A process as claimed in any of the preceding claims wherein the amount of phosphoric acid used is equivalent to 174 g of P_2O_5 per 100 g of zinc oxide.

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6. A process as claimed in any of the preceding claims wherein at stage (a) zinc oxide is reacted with phosphoric acid at 150°C for 30 min.
7. A process as claimed in any of the preceding claims wherein at stage (b) the reacted mass from stage (a) is heated at 300°C for 60 min.
8. A process as claimed in any of the claims 1 to 7 wherein the reaction is continued at 300°C until the weight loss due to dehydration corresponds to 14.5% of the original weight of $\text{ZnO} + \text{H}_3\text{PO}_4$.
9. A process as claimed in any of the preceding claims wherein at stage (c) the reacted mass from stage (b) is treated with water and ground to a paste.
10. A process as claimed in claim 9 wherein the amount of water used is 250 ml per 100 g of zinc oxide.
11. A process as claimed in any of the preceding claims wherein at stage (d) the basic compound used is lime.
12. A process as claimed in claim 11 wherein 56 g CaO is used for every 100 g of ZnO in the mixture.

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13. A process as claimed in any of the claims 1 to 10 wherein at stage (d) the basic compound used is calcium carbonate.
14. A process as claimed in claim 13 wherein 100 g of CaCO_3 is used for every 100 g of ZnO in the mixture.
15. A process as claimed in any of the claims 1 to 10 wherein at stage (d) the basic compound used is a solution of ammonia.
16. A process as claimed in claim 15 wherein 34 g NH_3 is used for every 100 g ZnO in the mixture.
17. A process as claimed in any of the preceding claims wherein at stage (d) the reaction mass, after neutralisation, is allowed to stand for at least six hours prior to drying.
18. A process as claimed in any of the preceding claims wherein at stage (d) the quantity of the basic compound that is added is sufficient to raise the pH of the mixture to 3.0.
19. A process for the manufacture of slow-releasing zinc fertilizer substantially as herein described and as illustrated in the Example(s).

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13 August 1990

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